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(71) Applicants
Toppan Printing Co. Ltd.
5-1, 1-chome,
Taito,
Taito-ku,
Tokyo,
Japan.
(72) Inventors
Akira Yoshikawa,
Kazuhiko Ohta.
(74) Agents
A.A. Thornton & Co.,
Northumberland House,
303-306 High Holborn,
London,
WC1V 7LE.

(54) A decorative laminate and a manufacturing method therefor

(57) A laminated thermosetting decorative laminate (2) has a three-dimensional pattern on its surface which consists of protruding parts and recessed parts forming smooth curves. This decorative laminate is manufactured by using a press plate having an enamel layer (6) on the surface of a metal substrate (5).

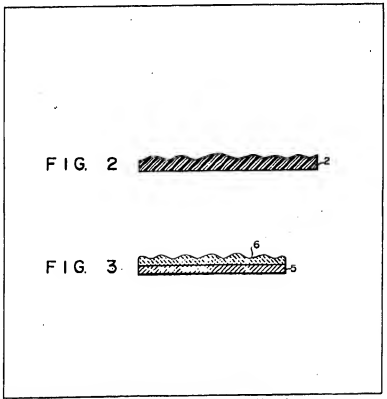

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FIG. 1

FIG. 2

FIG. 3

FIG. 4

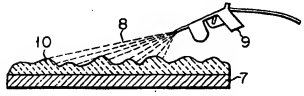

FIG. 5

FIG. 6

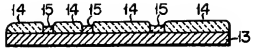

FIG. 7

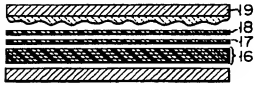

FIG. 8

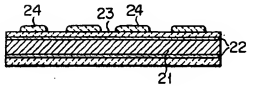

FIG. 9

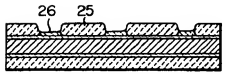

FIG. 10

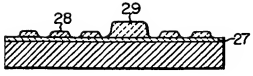

FIG. 11

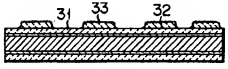

FIG. 12

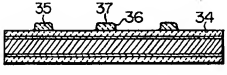

FIG. 13

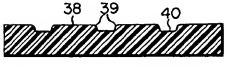

FIG. 14

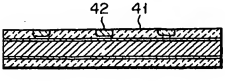

FIG. 15

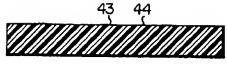

FIG. 16

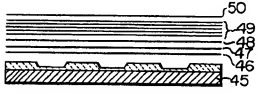

FIG. 17

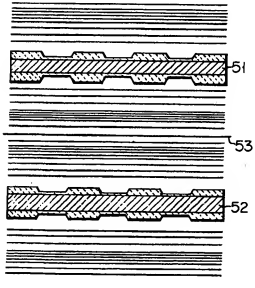

FIG. 18

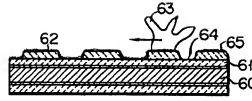

FIG. 19

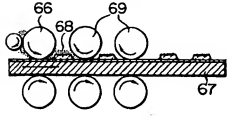

FIG. 20

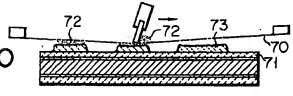

FIG. 21

SPECIFICATION

A decorative laminate and a manufacturing method therefor

The present invention relates to a decorative laminate using thermosetting resin and a manufacturing method therefor.

Decorative laminates can provide various surface shapes, colors, glosses and volumes resembling wood, enamel, pottery, tile, cloisonne ware, natural stone and so on, and they are widely used as raw materials for furniture and building materials. These kinds of decorative laminates are manufactured by impregnating a printed decorative sheet having e printed wood grain or a printed enamel pattern with a thermosetting resin; laminating the printed decorative sheet with core papers, an overlay paper or the like; and hot pressing the laminated body using a predeterminad embossing press plate.

For forming a three-dimensional pattern or a roughened surface for reducing gloss, methods heve been proposed such as embossing using an etched or sand blasted metal press plate. However, the procedure for manufacturing such a metal press plate is complex, and the derived metal press plate is extremely expensive. Thus, it has been general practice to manufacture resin press plates using e metal press plate as an original, and to use these resin press plates for actual embossing. However, a resin press plate of, for exemple, phenol resin or epoxy resin is defective in that a release sheet must be used to prevent adhesion between the plate and the decorative laminate. Its durability has not been satisfactory, either. Further, for various decorative laminates of thermosetting resin, a printed decorative sheet is used which has a printed pattern of an abstract pattern, wood texture, stone grain, e pattern of brick or ceramic, or various other patterns. Even when this printing is very fine, the design of the decorative laminate may not be satisfactory if the resin layer at the surface of the decorative laminate does not have a three-dimensional pattern or e gloss which goes well with the printing. Especially in the case of a wood grain patterned decorative laminate, it has been difficult to completely align the part of the printed decorative sheet representing the xylem vessels (hereinafter called the tracheal part) with the recess formed by embossing. For manufacturing this kind of decorative laminate, a so-called wiping method is known according to which a decorative laminate is molded using a press plate with a three-dimensional pattern formed by etching the surface of a metal plate such as stainless steel; then the recess of the derived decorative laminate is painted with ink for coloring the tracheal part. However, with this method, it is extremely difficult in practice to select an ink which strongly adheres to the surface of the decorative laminates and which still presents the other required properties. For example, even when e transparent resin is coated over the ink layer for protecting the ink layer, it is very difficult to obtain the original surface conditions and properties of the decorative laminate of thermosetting resin. Further, in a metal press plate manufactured by etching or sand blasting, the inclination of the protruding and recessed parts is sharp, the protruding part is generally smooth, and the recessed part is rough. Thus, decorative laminates manufactured using such a metal press plate heve been defective in their reproduction of the surfaces of the enamel and the natural materials.

The primary object of the present invention is, therefore, to provide a laminated thermosetting decorative sheet with improved design.

Another object of the present invention is to provide e method for manufacturing a laminated thermosetting decorative sheet using a press plate which is improved in releasing ability and durability and which is inexpensive.

The present invention provides a decorative laminate which has a smooth three-dimensional pattern and which preferably has a varied surface luster or gloss pattern due to the formation of a rough part.

As a preferred embodiment of the present invention, a decorative laminate is provided which is shaped in continuous curves formed by alternate protruding parts and recessed parts.

As another preferred embodiment of the present invention, a decorative laminate is provided in which the protruding parts formed on the surface heve lustar, the shoulders of the protruding parts are smooth and curved, and the bottoms of the recessed parts are roughened and which may be used as a decorative laminate of a tile pattern.

As a further preferred embodiment of the present invention, a decorative laminate is provided in which the bottoms of the recessed parts of the surface are roughened and colored. This decorative laminate is suitable as a decorative laminate with wood grain using the above-mentioned recessed parts as the tracheal parts or one with a designed tile pattern.

A decorative laminate according to the present invention may be easily manufactured using a press plate having an enamel layer formed on a metal substrate, this enamel layer having e three-dimensional pattern or a rough surface.

This invention can be more fully understood from the following detailed description when taken in conjunction with the accompanying drawings, in which:

Figure 1 is a schematic sectional view of a conventional decorative laminate;

Figure 2 is a schematic sectional view of a decorative laminate according to an embodiment of the present invention;

Figure 3 is a schematic sectional view of an embossing press plate having an enamel layer and used in the present invention;

Figure 4 is a schematic view illustrating an embodiment of a method for manufacturing an embossing

press plate having an enamel layer;

Figures 5 and *6* are sectionel views illustrating embodiments of an embossing press plate having an enamel layer;

Figure 7 is a schematic sectional view illustrating a method for hot pressing a decorative laminate elements with the press plate shown in Figure 3;

Figures 8, 9 and *10* are sectional views illustrating other embodiments of an embossing press plate having an enamel layer;

Figures 11 and *12* are sectionel views illustrating embodiments of an embossing press plate having an enamel layer with roughened protruding parts;

Figure 13 is a sectional view of a decorative laminate manufactured with the embossing press plate shown in Figure 12;

Figure 14 is a sectional view illustrating an embodiment of an embossing press plate having an enamel layer with a roughened surface;

Figure 15 is a sectional view illustrating a decorative laminate manufactured with the embossing press plate shown in Figure 14;

Figures 16 and *17* are schematic sectional views illustrating methods for hot pressing a decorative laminate elements with an embossing press plate having an enamel layer;

Figures 18, 19 and *20* are schematic sectional views illustrating methods for adhering a colorant on roughened protruding parts of an enamel layer; and

Figure 21 is a sectional view of a decorative laminate in which the recessed parts are roughened and colored.

As may be seen from Figure 1, in the surface of a decorative laminate 1 manufactured with a conventional metal or resin press plate, the sharp protruding and racessed parts of the press plate is reproduced and a smooth pattern of a protruding and recessed parts cannot be obtained. To the contrary, as shown in Figure 2, a decorative laminate 2 according to the present invention has a smoother surface than a conventional decorative laminate. Therefore, the decorative laminate of the present invention is advantageous in that its three-dimensional surface is smooth and suitable for reproducing three-dimensional patterns resembling enamel, pottery, tiles, cloisonne ware, natural stone and so on.

The decorative laminate of the present invention is manufactured with a press plate or an embossing plate which has an enamel layer 6 on a metal substrate 5 of steel, cast iron, copper, aluminum, steinless steal or the like as shown in Figure 3. The enamel layer 6 is formed by coating the substrate with a general glaze and firing it. A press plate suitable for manufacturing a decorative laminate of various patterns is manufactured by forming a three-dimensional pattern and a luster pattern, that is, roughened parts on the surface of the enamel layer. The press plate having the enamel layer has been proved to be advantageous in manufacturing a laminated thermosetting decorative sheet in the following respects:

(1) A sufficient releasing ability is obtained with thermosetting resins such as melamine formaldehyde resins since the surface of the enamel layer is very hard and fine.

(2) Formation of protruding parts on the surface of the enamel layer may be relatively easily accomplished, for example, by means of screen printing with frit ink.

(3) Roughening the protruding parts may be easily accomplished by methods such as mixing a melting agent into the frit ink.

(4) The bottom surface of recessed parts of the enamel layer is very smooth so that a colorant such as ink adheres only slightly and may be removed easily. Thus, adhesion of the colorant only to the roughened surface of the protruding parts may be easily accomplished.

(5) A decorative laminate with a colored pattern completely corresponding to the three-dimensional pattern of the plate may be obtained since the colorant adhering to the roughened surface is completely transferred to the recessed parts of the decorative laminate when an enamel coated press plate with roughened and colored protruding parts is used.

(6) The colorant transferred to the decorative laminate is bonded to it due to the melting of the thermosetting resin of the decorative laminate.

Although the press plate is described with reference to a plate shape, it may take a roll shape.

The process of forming recessed parts and protruding parts on the enamel layer of the press plate will be described. For forming smooth recessed parts and protruding parts on the enamel surface of the substrate, a method as shown in Figure 4 is possible according to which a glaze 8 is sprayed by a spray gun 9 onto the surface of a substrate 7 and then fired to form a surface 10 with a random three-dimensional pattern. Alternatively, as shown in Figure 5, after uniformly applying a glaze on the three-dimensional pattern of a substrate 11, a three-dimensionally patterned surface 12 is formed by firing. Still alternatively, as shown in Figure 6, glazes of more than one kind with different melting points are applied to the surface of a substrate 13 in a pattern or at random. A three-dimensional pattern is formed by firing at a temperature capable of firing the glaze 14 of the highest melting temperature and by melting the glaze or glazes 15 of lower melting temperature. The surface of a decorative laminate embossed with a press plate manufactured in one of these manners has a smooth three-dimensional pattern as shown in Figure 2.

A decorative laminate with a continuous curved surface formed by alternate recessed parts and protruding parts will be decribed as a preferred embodiment of a decorative laminate manufactured with a press plate having an enamel layer with a smooth three-dimensional pattern.

The press plate to be used in this embodiment may be prepared by pre-treating a metal substrate with processes such as degreasing; using a spray gun to coat the substrate with a slip obtained by adding a mill addition agent and water to a glass frit and grinding and kneading the mixture in a ball mill; and firing the coated substrate. The frit to be used may be of the general kind and has as its main components, for example, SiO_2, Al_2O_3, B_2O_3, Na_2O, K_2O, CaO, ZnO, MgO and the like. The mill addition agent may be a suspending material such as clay, an emulsifying material such as tin oxide, a colorant borax or an electrolytic material such as magnesium carbide. The firing is performed at a temperature higher than the melting temperature of the frit, generally in the range of 500 - 900°C. The molten frit is in the form of a viscous liquid so that the surface tension tends to minimize the surface area. This, together with the flowability of the molten frit, serves to soften the sharpness of the recessed and protruding parts to form rounded recessed and protruding parts. It is possible to obtain the most suitable flowability and the same roundness at the recessed and protruding parts by appropriately selecting the composition of the frit and the temperature conditions. Thus, an enamel layer which smoothly conforms to the surface of the metal substrate and which has recessed parts and protruding parts of similar dimensions may be obtained. Although the three-dimensional pattern of the enamel layer of the press plate and the three-dimensional pattern of the decorative laminate obtained by using the press plate are opposite, they are similar in outer appearance. Therefore, the three-dimensional pattern of the enamel layer may not have to be made opposite to the three-dimensional pattern of the decorative laminate to be manufactured. Thus, it is possible to obtain a press plate which has a sinusoidally curved surface formed by alternate recessed parts and protruding parts, that is, a horizontally symmetrical curve.

A laminated thermosetting decorative sheet is manufactured by a conventional method using such a press plate. The thermosetting resin to be used here may be a melamine formaldehyde resin, diallylphthelate resin, a polyester resin, a guanamine resin or the like. As shown in Figure 7, a decorative laminate elements such as core papers 16 impregnated with resin, a printed decorative sheet 17 on which is printed a desired pattern and which is impregnated with resin, and an overlay paper 18 impregnated with resin is laminated. A press plate 19 is placed thereover so that its enamel layer having a three-dimensional pattern is in contact with the overlay paper 18. Plywood may be used instead of the core papers as desired. A decorative laminate with a smooth three-dimensional pattern and with a luster corresponding to the enamel is obtained by hot pressing. This decorative laminate does not have sharp angles in the three-dimensional pattern so that it does not give an unnatural appearance, dust does not tend to collect at its recessed parts, and cleaning is easy.

Example 1

Treatments such as degreasing were performed on a steel plate of 1.6 mm in thickness. Slip was prepared which consists of frit having as its main components SiO_2, B_2O_3, Al_2O_3, Na_2O and the like; water; a suspending material such as GAIROME clay (fire clay); and other additives. Slip was sprayed with a spray gun on one surface of the steel plate to form a random three-dimensional pattern thereon. Firing at 850°C was performed for three minutes, and an embossing press plate having an enamel layer on its surface was obtained. This embossing plate was used for forming a decorative laminate of melamine formaldehyde resin. Thus, decorative laminate of melamine formaldehyde resin with a smooth three-dimensional pattern and improved luster were obtained. No defects were noted on the embossing press plate after over a hundred repeated embossings, regardless of the fact that hot pressing was performed at a temperature of 140°C and a pressure of 80 kg/cm^2.

Another method for forming a three-dimensional pattern on a press plate will be described. After forming an enamel layer by a conventional method on a metal substrate, protruding parts or recessed parts may be formed. For example, it is possible to print a protruding pattern on the surface of an enamel layer by screen printing using an ink having a glass content of over 10%, e.g., frit ink, and then firing. It is also possible to apply an adhesive in a desired pattern on the surface of the enamel layer, to scatter glass powder called frit thereover, and to fire after removing the frit on parts other than the pattern. It is further possible to form a protruding pattern on the surface of the enamel layer by using a transfer sheet with a pattern formed on a sheet such as a paper sheet or a plastic film by ink containing a pigment and frit and firing.

The method for forming a protruding part or a recessed part on the enamel layer of a press plate will now be described in more detail.

In the embodiment shown in Figure 8, ground coat layers 22 are formed on both surfaces of a metal substrate 21, although these ground coat layers are not essential. Formation of these layers is preferable since it improves both the adhesion between a cover coat enamel layer and the metal substrate and the durability of the press plate. It is further preferable to form a ground coat layer on the back surface of the metal substrate to prevent warping and corrosion of the press plate. A so-called black ground coat containing cobalt oxide may be used for the ground coat layers. After completing firing of the ground coat layers 22 and cooling the substrate, a cover coat enamel layer 23 is formed over each ground coat layer 22. For the cover coat enamel, a slip may be used, that is, a glaze which is prepared by adding a mill addition agent to a commercially available enamel frit and by grinding the mixture in a ball mill. The coating method may be arbitrarily selected. However, coating may be generally accomplished by spraying when the press plate has large dimensions. As in the case of the ground coat layers 22, an cover coat enamel layer 23 is

preferably formed on both surfaces of the substrate 21.

The finished conditions of the surface of the cover coat enamel layer may be varied by suitably selecting the kinds of frit and mill addition agent to be used, the viscosity of the slip when coated, the coating method, the firing temperature and the like. That is, a desired finished condition may be formed on the surface varying from an even condition to a slightly and smoothly waving condition. For forming a three-dimensional pattern, methods mentioned above may be adopted. Easy methods among these are to increase the viscosity of the slip, to degrade the leveling, or to enlarge the diameter of the drops of slip by decreasing the air pressure of the spray gun. In this case, fluctuations in the height of the pattern in the cover coat enamel layer need to be kept in a certain range since too much fluctuation tends to cause irregular transfer of ink on the layer in screen printing or in the transfer procedure. As for the luster of the surface of the cover coat enamel layer, an arbitrarily selected degree of luster may be obtained varying from a condition corresponding to e completely mirror surface to a completely matted surface. Matting of the surface of the cover coat enamel layer may be easily accomplished by adding a matting agent to the glaze or by lowering the firing temperature. Further, the surface conditions of the cover coat enamel layer may also be changed by suitably selecting glazes of different particle size or different melting points. In either case, the cover coat enamel layer should not be too thick, preferably below 500 μ. If it is too thick, it might lead to e breakage due to the pressure in hot pressing.

Methods for forming protruding parts 24 on the surface of the fired cover coat enamel layer 23 by screen printing or by transfer as in Figure 8 will be described in more detail.

The method utilizing screen printing will first be described. The printing screen may be one using a screen of 150 - 200 mesh or, more preferably for the present method, one using a thick screen of 60 - 70 mesh. In the latter case, since the thickness of the ink layer is great, the decorative laminate manufactured will have excellent three-dimensional effects. The mesh, wire diameter, thickness of the screen, screen material to be used and the like are determined according to the desired effects, the desired fineness of the pattern and so on, but a screen of 30 - 250 mesh using monofilament threads or multifilament threads of nylon or polyester is generally used. As for the screen ink, commercially available frit ink is used, that is, commercially available printing glass frit which is finely ground and kneaded in screen oil.

The method utilizing transfer will now be described. A predetermined patter of frit ink is printed on a surface of a base material such as a paper sheet or a film by a desired printing method such as the screen printing or photo gravure printing. Screen printing enables the printing of thick patterns, and photo gravure printing enables the printing of fine patterns. The transfer method may be arbitrarily selected from conventional methods such es a method for forming a varnish transfer layer on the surface of the cover coat enamel layer and for transferring by pressing, or a method for forming a varnish transfer layer on the surface of the transfer paper and for transferring it directly to the surface of the cover coat enamel layer. The transfer method is advantageous in that the transfer paper may be printed in advance and the actual transfer may be easily accomplished by the water transferring method or with a simple machine. However, the thickness of the formed ink layer is limited and the height of the raised ink layer is slightly inferior in comparison with the direct printing method of screen printing.

Modified embodiments of the method for forming a three-dimensional pattern by screen printing or transfer will be described hereinafter. In the embodiment shown in Figure 9, a pattern is printed by screen printing or by transfer on a cover coat enamel layer 25 using a frit ink higher in specific weight than the cover coat enamel layer 25. In firing, the temperature is raised to a point where the cover coat enamel layer 25 is melted. Then the frit ink part sinks into the cover coat enamel layer 25, thus forming recessed parts 26. Various finished surfaces may also be obtained by suitably combining the screen printing and transfer methods. Either of these two methods may be repeated for better effects. For example, more than one printing screens, each having a different thickness, may be used for varying the height of the protruding parts in several steps. The luster may also be varied by changing the ink composition. In manufacturing a press plate of this type, the transfer of the ink layer and the firing may be repeated, or firing may be performed after several transfers of the ink layer. Figure 10 shows an embodiment in which this method is utilized for forming low protruding parts 28 and a high protruding part 29 on a cover coat enamel layer 27. With such a press plate, a decorative laminate having recessed parts of different depths may be obtained.

Further, as shown in Figure 11, it is possible to have a matted surface 33 on a protruding part 32 formed on an enamel layer 31 of the press plate. The matting of the top surface of the protruding part may be easily accomplished by using a matting ink obtained by mixing a matting agent into the frit ink to be transferred to the enamel layer or the cover coat enamel layer by screen printing or by transfer. It is alternatively accomplished by mixing into the ink coarse particles of high melting point such as alumina or zirconium oxide. In this case firing must be performed at a temperature at which alumina or zirconium oxide does not melt. In order to emphasize the matted surface of the protruding part and to improve the design effects, the cover coat enamel layer 31 constituting the recessed parts are preferably smooth. The composition of the slip and the firing conditions must be considered so that the surface of the recessed parts may be as smooth as a mirror surface or over 50% in mirror reflectivity at an angle of incidance of 60°. However, the surface of the cover coat enamel layer need not be even and may have smooth undulations and swellings. A decorative laminate molded by the press plate shown in Figure 11 has a matted surface at the bottom of each recessed part and has a smooth surface at the protruding parts and is thus superior in design. With a conventional etched metal press plate, the recessed part becomes matted, and the protruding parts of the derived

decorative laminate are thus matted while the recessed parts are smooth. It is difficult to manufacture a decorative laminate as obtained in accordance with the present invention with this type of press plate.

Several embodiments of a decorative laminate having such matted surfaces will be described. In the first embodiment, as shown in Figure 12, a raised ink layer is printed on the surface of a cover coat enamel layer 34 with a thick printing screen using a frit ink containing a matting agent. By firing at a suitable temperature, sides 36 of protruding parts 35 are melted and joined with the cover coat enamel layer 34 to form a shiny surface. Top surfaces 37 alone are matted. A decorative laminate manufactured with the press plate shown in Figure 12 has round shoulders 39 of shiny protruding parts 38 and matted surfaces at the bottom of recessed parts 40. A decorative laminate having a tile pattern is easily obtained with this method. Such a decorative laminate may be manufactured with a press plate made by printing a part corresponding to the joint of the tiles using a frit ink containing a matting agent and then firing. This decorative laminate is very similar to real tiles as the parts corresponding to the shoulders of the tiles are rounded and the joint parts are matted.

The second embodiment is shown in Figures 14 and 15. As shown in Figure 14, it is possible to form an ink layer 42 which is of the same level as a cover coat enamel layer 41 and which is matted on the surface by adjusting the specific weight of the frit ink containing a matting agent or by adjusting the firing temperature. A decorative laminate manufactured with this press plate is shown in Figure 15. Its surface is substantially even but has partially matted parts 43 and shiny parts 44. Thus it is suitable as decorative laminate having a pattern of natural stone or the like.

The method for manufacturing a laminated thermosetting decorative sheet with a press plate having a matted surface manufactured in the manner described above is not basically different from those methods mentioned earlier. The manufacturing method will be described with reference to Figure 16 taking a decorative laminate of melamine formaldehyde resin as an example. Over an enamel layer of a press plate 45 are placed in the order named: an overlay paper 46 impregnated with melamine formaldehyde resin, a printed decorative sheet 47 similarly impregnated with melamine formaldehyde resin, a barrier paper 48 similarly impregnated with melamine formaldehyde resin as needed, a required number of core materials 49 impregnated with phenol resin, and a warping-preventive sheet 50. Several such combinations are stacked and are put with cushions in a hot press for hot pressing. The rear surface of the press plate is in contact with the rear surface of the decorative laminate to be manufactured. Thus, if an enamel layer is also formed on the rear surface of the press plate, it is advantageous in that a special release paper or a release film is not required since the enamel layer has releasing ability.

The pressing conditions may be the same as in the case of a conventional method for manufacturing a decorative laminate of melamine formaldehyde resin and need not require special consideration. The preferred temperature is, at maximum, 140 - 160°C, the pressure is 50 - 120 kg/cm^2, the heating time is 15 - 30 minutes, and the cooling time is 15 - 30 minutes.

Protruding parts of an ink layer may be formed on the enamel layer on the rear surface of the press plate so that both surfaces of the press plate may be used for manufacturing decorative laminates. Then, since the decorative laminate elements can be placed at both sides of the press plate, the required number of press plates 51 may be made half the general case in press e stack of elements. The number of decorative laminate elements which may be pressed at the same time may be increased due to this. In this case, two sets of decorative laminate elements such as the overlay paper sheet, the printed decorative sheet, the core material sheets and so on may be placed between the press plate 51 and a press plate 52. A release paper sheet 53 should be interposed between each such set.

Example 2

A cold rolled steel plate of 1.6 mm in thickness for forming an enamel layer was cut into predetermined dimensions, and degreasing, pickling and water rinsing were performed thereafter.

Black ground coat having the composition shown below was uniformly sprayed on both surfaces of the steel plate. After drying, the plate was fired, under the condition that a maximum temperature of 870°C was maintained for 3 minutes.

Black ground coat composition:

Ground coat frit	100 parts by weight
GAIROME clay	7 parts by weight
Feldspar	3 parts by weight
Borax	0.75 parts by weight
Magnesium carbonate	0.25 parts by weight
Water	40 parts by weight.

White cover coat enamel of the composition shown below was uniformly sprayed over both surfaces of the steel plate to which had already been applied the ground coat. After drying, firing was performed under the condition that a maximum temperature of 850°C was maintained for 2 minutes.

White cover coat enamel composition:

Cover coat enamel frit	100 parts by weight
GAIROME clay	5 parts by weight
Tin oxide	8 parts by weight
Magnesium carbonate	1 part by weight
Water	50 parts by weight

The surface of the derived cover coat enamel layer had excellent luster and smoothness. Parts corresponding to the joints of hexagonal tiles were printed on this cover coat enamel layer surface using a printing screen of 70 mesh. The ink was prepared by kneading screen oil with a commercially available printing frit (already ground) with matting agent added. The firing was performed under the condition that a maximum temperature of 750°C was maintained for 2 minutes. The edges of the ink parts were shiny and rounded by melting, and the tops of the ink parts were matted. The ink layer also formed protruding parts integral with the cover coat enamel layer to be obtained a press plate. A decorative laminate of melamine formaldehyde resin was press using the press plate. As a printed decorative sheet, a titan paper sheet with a printed pattern of tiles was prepared in advance. Hot pressing was performed by the conventional method. The pressing conditions of the hot-cold method were: 145°C maximum temperature, 20 minutes heating, 80 kg/cm^2 pressure, and 20 minutes cooling. The release sheet was not used. The decorative laminate thus obtained had a well matched, smooth, enamel-like surface with a printed pattern on the protruding parts and matted parts corresponding to the joints of tiles; these parts closely resembled the real joints of tiles. This decorative laminated sheet of melamine formaldehyde resin as a whole presented an outer appearance which closely resembled the real surface of tiles. The press plate endured over a hundred repeated pressings.

Example 3

Screen printings of the combination shown below were performed on the surface of a cover coat enamel layer obtained in a method similar to that of Example 2.

No.	Screen Mesh	Pattern	Ink
1	150 mesh	Stone grain texture	Shiny
2	60 mesh	Modified tile joint	Matting

After completing the No. 1 printing, the ink layer was dried by heating to 100°C. After drying, the No. 2 printing was performed. Firing was then performed to integrate the ink layer with the cover coat enamel layer. The firing conditions were the same as in Example 2. The surface of the press plate thus obtained was shiny and protruded slightly at parts corresponding to stone grain texture; it was highly raised and matted at parts corresponding to tile joints; and it was rounded and shiny at the shoulders of the protruding ink layer. A decorative laminate of melamine formaldehyde resin was molded with this enamel plate as a press plate under the same conditions as in Example 2. The obtained decorative laminate had, at parts, an appearance similar to the joints of tiles and had fine stone grain texture on parts corresponding to the surface of the tiles. Thus, the outer appearance resembled that of the real tiles more than in the case of Example 2.

Example 4

A diallylphthalate impregnated paper sheet was placed over a plywood board of 4 mm in thickness. Hot pressing was performed using the press plate obtained in Example 2 at a temperature of 130°C and a pressure of 10 kg/cm^2 for 10 minutes. The press plate released without the use of a release sheet. The decorative laminate of diallylphthalate had an appearance similar to that of the decorative laminate obtained in Example 2.

Example 5

In manufacturing the press plate of Example 3, the stone grain texture was printed on transfer paper sheet in advance. This printed pattern was transferred to the surface of the cover coat enamel layer. One printing process was thus eliminated by this transfer. The press plate obtained had the same finish as in case of Example 3.

Example 6

Black ground coat (SG-O manufactured by Nihon Frit Co., Ltd.) was uniformly applied to both surfaces of a pre-treated steel plate of 1.6 mm in thickness for forming an enamel layer. Firing was performed under the condition that a maximum temperature of 870°C was maintained for 3 minutes. Semi-matting white cover coat enamel (manufactured by Nihon Frit Co., Ltd.) was also applied to both surfaces of the plate. Firing was again performed under the condition that a maximum temperature of 750°C was maintained for 2 minutes. Printing of parts corresponding to the tracheal parts of wood grain was performed with a matting ink using a printing screen of 200 mesh on the surface of the cover coat enamel. Firing was performed again under the

condition that e maximum tempereture of 730°C wes meintelned for 2 minutes. The enamel plate thus obtelned wes semi-metted at the surface of the cover coet enamel, and completely metted et parts corresponding to the tracheal parts of the wood grain. The shoulders of the ink layer were not rounded, but remained sharp. The enamel plate thus obtained wes usad as e press plate. Hot pressing was performed by the conventionel method using e printed decoretive sheet with the printed pattern of e Jepenese oak and impregnated with melamine formeldehyde resin (Nika Resin manufactured by Nihon Carbide Industries Co., Inc.). The decoretive laminate of melamine formeldehyde resin thus obtained had recessed tracheal parts. These tracheal parts ware metted, providing a decoretive laminata superior in design.

In accordance with the present invention, it is possible to manufacture a decorative leminete in which a colorant is fixed to the recessed perts by using a press plete which holds the colorant in the metted parts of the protruding perts formed on the enemal layer of the press plate.

The colorant to be used may be selected freely if it is compatible with the molten thermosetting resin in the molding process, end it may be a single pigment. Verious studies heve been made in considertion of the durebility of the decorative laminete obteined. As e result of such studies, it hes been proved that the colored parts of the obtained decoretive laminate ere stable if a colorant is used which contains, in addition to the coloring components such as pigments, a resin as a binder, this resin being the same thermosetting resin used for the decorative leminata, or e thermosetting resin which is compatible with such a thermosetting resin of the decoretive leminate and which has lower curing tamparatura then that of the thermosetting resin of the decorative laminete. The results of a test of the adhesion of the verious colorants fixed by the above-mentioned method to the decorative laminate of melamine formaldehyde resin are shown in Table 1. The evaluations concern the degree of fading after sweeping the colored part of the decorative laminate 100 times with e cloth wet with lecquer thinnar.

TABLE 1

Colorant	*Binder*	*Nature*	*Durability of the decorative laminate*
Ink A for decorative laminate	Cellulose based resin	Liquid (soluble in oil)	poor
Ink B for decorative laminete	Cellulose or acryl besed resin	Liquid (soluble in weter)	fair
Screen Ink A	Alkyd resin	Liquid (soluble in oil)	fair
Screen ink B	Alkyd resin, melemine resin	Liquid (soluble in oil)	good
Sampte ink A	Melamine resin	Liquid (soluble in water)	good
Sample ink B	Epoxy resin	Liquid (soluble in oil)	good
Pigment A	None	Powder	poor
Pigment B	Vinyl resin	Powder	poor
Powder paint A	Polyamide resin	Powder	poor
Powder paint B	Polyester resin	Powder	fair
Sample toner	Melemine resin	Powder	good

As mey be seen from the above table, it was found that, in the case of a decorative laminate of melamine formaldehyde resin, the resistance of the colored parts to thinner is improved by using a colorant containing, as a binder, a thermosetting resin such as a melamine formaldehyde resin or an epoxy resin. In the case of the powder paint B in Table 1, although the binder was thermosetting, sufficient curing was not obtained since the curing temperature was higher than the pressing temperature of the decorative laminate of melamine formaldehyde resin. This relation between the resin of the decorative laminate and the binder is applicable to decorative laminates of other thermosetting resins such as diallylphthelate end polyester resin. The colorent containing the coloring components and a binder may be in liquid form or in powdered form. However, the powdered form is preferable since it may be aesily removad from the smooth parts of the press plate.

A method for holding the colorant in only the matted parts of the enemel layer of the press plate will be described. The so-called wiping method is easiest and preferable. As shown in Figure 18, a colorant 62 is applied to the entire surface of an enamel layer 61 of a press plate 60, and the surface is wiped with a cloth or a paper sheet 63. The colorant on a smooth part 64 is thus removed. Wiping is easy if the cloth or paper sheet is wet with a solvent of the colorant used. Although the colorant on the smooth part 64 of the enamel layer is eesy to wipe away, it is herd to wipe off a matted part 65 since the colorant eats into the fine recesses on the surface. In real manufacture, wiping of the press plate herd to accomplish manually since the press plate is quite large. Thus, it is preferable to use a wiping machine as shown in Figure 19. As shown in Figure 19, e colorant 68 is applied to the entire surface of a press plate 67 by e coating roll 66. It is wiped awey by a wiping roll 69 rotating in opposition to the movement of the press plate 67. When the colorent is a liquid, a wiping roll of rubber is used. When the colorant is a powder, a soft material such as a cotton roll is used for the wiping roll. With this method, wiping can be accomplished over the entire surface of a press plate of large area in a uniform menner, and the colorant is left only on the matted part. The technique of screen printing may alternatively be used. As shown in Figure 20, e screen plate 70 used for forming matted parts 73 on the surface of an enamel layer 71 is fixed on the anamel layer 71 so that the line drawing parts of the printing screen 70 and the matted parts 73 of the enamel layer 71 are eligned. A colorant 72 is printed by screen printing so that matted parts 73 elone are colored. The particular printing screen used for forming the matted parts is not required; a separate printing screen made from the same positive pattern may elternetively be used. Especially when the printing screen used for forming the matted parts is of low mesh and great thickness, the same printing screen is not preferable since too much colorant is then applied. Thus, better results are obtained when a separate printing screen is prepared which is less thick and around 200 mesh. Further, when the positive used for forming the matted parts is not used, but a corrected positive with slightly narrower line drawing parts is used for manufacturing e printing screen, workability is improved since then the colorant does not leak out from the matted parts of the enamel layer.

Further, it is possible to apply more than one color by dividing the matted parts between more than one printing screen and coloring the matted perts with colorants of different hues. The decorative laminata thue obteined is colored in more then ona color and is ornamentally improved.

In eny of the above methods for applying a colorant or colorants to the matted parts by the wiping method or the screen printing method, the water or volatile material such as a solvent in the colorant attached to the matted parts of the enamel layer is removed by thorough drying when a liquid colorant is used. When too much of such materials remain, they are evaporated in the pressing process of the decorative laminata and might lead to surface irregularities or blisters of the decorative laminate. Such consideration need not be made when e powdered colorant is used.

It is thus possible in this manner to mat and color the recessed parts of e decorative laminate of thermosetting resin by using e press plate holding a colorant or colorants only on its matted parts. The pressing method of the decorative laminate is not different from that described with reference to Figures 7, 16 and 17. The thermosetting resin, melted once in the process of heat pressing the decorative laminate, forms recessed matted parts when pressed by the protruding matted parts of the enamel layer of the press plate, and at the same time is combined with the colorant applied to the protruding matted parts of the enamel layer of the press plate. By curing the thermosetting resin, the colorant is securely attached to the recessed matted parts of the decorative laminate and does not remain on the enamel layer of the press plate. Thus, the press plate may immediately be returned to the process of applying a colorent for e next pressing procedure. The decorative laminate thus obtained is shown in Figure 21. This decorative laminate has smooth protruding parts 75, and the bottoms of recessed parts 76 are matted and colored e desired color by e colorant 77. Thus the obtained decorative laminate is vastly superior in design. In particular, when a printed decorative sheet with a tile or stone pattern is used together with matted parts of an enamel layer of matched sand grain or tile joint pattern (embossed pattern), the obtained decorative laminate closely resembles the real tile or ceramic finish and is superior in design. More preferably, when e printed decorative sheet of wood grain pattern is used together with matted parts of the enamel layer of e press plate having e trecheal pattern, a decorative laminate is obtained whose recessed parts are colored the color of the trecheal part. In the decorative laminate of wood grain thus obtained, the trecheal recessed parts and the colored parts are completely aligned, unlike in the case of the conventional method according to which the color of the tracheal parts is printed on the printed decorative sheet. Thus, this decorative laminate of wood grain is far superior in design and is capable of reproducing the pattern of natural wood grain faithfully.

Example 7

An extremely low carbon steel plate of 1.6 mm in thickness for forming an enamel layer was cut to a predetermined size and thereafter degreased, pickled, and rinsed with water. Black ground coat was sprayed on both surfaces of the steel plate. After drying, firing was performed under the condition that the maximum temperature of 870°C was maintained for 3 minutes. White cover coat enamel was similarly applied thereover on both surfaces. After drying, firing was again performed under the condition that the maximum temperature of 850°C was maintained for 2 minutes. The surface of the cover coat enamel layer thus obtained was shiny and smooth. Parts corresponding to the joints of hexagonal tiles were printed on the surface of the cover coat enamel layer using a printing screen of 70 mesh. The ink was prepared by pulverizing screen oil with a commercially available printing frit with a matting agent added (already ground). Firing was performed under the condition that the maximum temperature of 750°C was maintained for 2 minutes. The edges of the inked parts were rounded and became glossy. The tops of the inked parts were matted. The inked parts protruded from the cover coat enamel layer and were formed integrally therewith.

A colorant of the composition shown in Table 2 below was applied to the surface of a press plate manufactured by the above method. The colorant was wiped away with a cloth wet with water, and the colorant remained only on the matted parts.

TABLE 2

Melamine resin (Nike Resin S-260 manufactured by Nihon Carbide Industries Co. Inc.)	100 parts by weight
Carbon black	4 parts by weight
Iron oxide based yellow pigment	16 parts by weight
Iron oxide based red pigment	5 parts by weight
Water	100 parts by weight
Surface active agent	2 parts by weight
Thickener	2 parts by weight

A melamine decorative laminate was molded using a press plate having an enamel layer with a colorant attached only to the matted parts after drying the water content in the colorant. A titan paper with a printed tile pattern was used as the printed decorative sheet, and hot pressing was performed by the conventional method. The hot-cold molding method was adopted at a maximum temperature of 145°C, a heating time of 20 minutes, a pressure of 80 kg/cm^2, and a cooling time of 20 minutes. No release sheet was used. The decorative laminate obtained had protruding parts of smooth surface with luster similar to that of the enamel and a matched printed tile pattern, and recessed parts with a matted surface and a resistered colored pattern. The decorative laminate obtained as a whole was superior in design. Its outer appearance was extremely similar to that of a real tile pattern. In the colored recessed parts, the colorant became integral with the melamine formaldehyde resin and adhered strongly, so that no disorders were noted after the decorative laminate was wiped a hundred times with a cloth wet with a thinner. Further, the colorant was completely transferred to the decorative laminate in the molding procedure, and no colorant remained on the surface of the enamel layer after the mold was opened.

Example 8

As in Example 7, a screen plate was used as a means for applying a colorant to the enamel layer of a press plate. The screen was made from a nylon screen of 200 mesh using, as a positive pattern, a hexagonal tile pattern which was previously used for forming a matted surface on the press plate. The coloring of the matted surface of the decorative laminate was extremely easy with this method, enabling coloring of higher concentration.

Example 9

A melamine decorative laminate was manufactured by a method similar to that of Example 7, except that the colorant of the composition shown in Table 2 was dried and ground in advance to be applied in a powdered form. The application of the colorant was much easier and smoother than in the case of a liquid colorant. The durability of the colored parts of the decorative laminate obtained was equivalent to that of the laminate obtained in Example 7.

Example 10

Screen printings of the combinations shown in Table 3 below were performed with frit ink on the surface of the cover coat enamel layer of a press plate obtained by the same method as in Example 7.

TABLE 3

No.	*Screen mesh*	*Pattern*	*Frit ink*
1	150 mesh	Stone grain texture	Matting
2	60 mesh	Modified tile joint	Matting

After the No. 1 printing, the ink layer was dried by heating to 100°C. Then after the No. 2 printing, firing was performed to adhere both ink layers to the cover coat enamel layer. The firing conditions were the same as in Example 7. In the surface of the enamel layer of the press plate thus obtained, the parts corresponding to the stone grain texture were matted and protruded slightly; the parts corresponding to the joints of the tiles were matted and protruded higher than the stone grain texture parts; and the shoulders of the ink layer were rounded and shiny.

Printing screens of 200 mesh were manufactured with the positive patterns used in the respective No. 1 and No. 2 printings above. Using each of these printing screens, the matted surface of the enamel layer of the press plate was colored according to Table 4 shown below.

TABLE 4

No.	*Screen mesh*	*Pattern*	*Colorant*
1'	200 mesh	Stone grain texture	Light gray
2'	200 mesh	Modified tile joint	Black

The composition of the colorant was as shown below:

TABLE 5

No. 1' colorant (light gray)

Melamine formaldehyde resin (S-260)	100 parts by weight
Carbon black	2 parts by weight
Titanium dioxide	23 parts by weight
Water	100 parts by weight
Surface active agent	2 parts by weight
Thickener	2 parts by weight

No. 2' colorant (black)

Melamine formaldehyde resin (S-260)	100 parts by weight
Carbon black	25 parts by weight
Water	100 parts by weight
Surface active agent	2 parts by weight
Thickener	2 parts by weight

After drying the colorants, a melamine decorative laminate was manufactured with this press plate. The decorative laminate of melamine formaldehyde resin obtained was matted and colored black in the tile joint parts; and was smooth with fine matted recesses and colored gray in the tile surface parts. The decorative laminate as a whole was superior in design, and presented an appearance which extremely resembled the

surface of real tiles.

Example 11

The press plate used in Example 7 and the colorant of the composition shown in Table 6 were used for applying a colorant to the matted surface of the press plate. A paper sheet impregnated with diallylphthalate resin was placed on a plywood of 4 mm in thickness, and hot pressing was performed at 130°C and 10 kg/cm² for 15 minutes.

TABLE 6

Diallylphthalate resin prepolymer	93 parts by weight
Diallylphthalate resin monomer	7 parts by weight
Pigment	25 parts by weight
Solvent (Acetone: MIBK 1:1)	100 parts by weight

The mold was released with ease without using a mold releasing film. The DAP decorative laminate thus obtained had an outer appearance similar to that of the decorative laminate of melamine formaldahyde resin obtained in Example 7, and the adhesion of the colorant to the matted surface of the recessed parts was sufficiently strong.

Example 12

A ground coat was applied to both surfaces of a steel plate 1.6 mm thick. Firing was performed in such way that the ground coat became smooth on either surface of the steal plate. Then, a cover coat enamel was applied on both ground coat layers for forming an enamel layers. Firing was performed for the second time in such way that the cover coat enamel became a smooth semi-gross enamel layer. The cover coat enamel consisted of 10 parts by weight of matting agent and 100 parts by weight of frit. It exhibited a mirror reflectivity of about 70%.

Using a 150-mesh printing screen and a frit ink for forming a completely matted enamel layer, a walnut tracheal pattern was printed on one of the enamel layers made from the cover coat enamel. Firing was performed for the third time, thereby obtaining a press plate with a matted protruding parts about 5 microns thick. The press plate was then coated on the enamel layer with a charcoal ink. It was wiped with a felt blanket, leaving the charcoal ink only in the matted surface of the protruding parts which correspond to tracheal parts of the pattern. The charcoal ink consisted of alkyd resin, melamine resin, colorant and solvant.

Thereafter, a melamine decorative laminate was formed, using the press plate and a titanium paper printed with a walnut tracheal pattern and impregnated with a melamine formaldahyde resin. The laminate thus obtained had recessed tracheal parts which were colored charcoal. Its surface strikingly resembled that of a real walnut plate with the so-called "open-pore finish".

Example 13

A press plate was obtained exactly in the same way as in Example 12, except that a 60-mesh printing screen was used to lay a protruding parts about 100 microns thick which correspond to an oak tracheal parts. The press plate was coated on an enamel layer with a charcoal ink. It was then wiped with a felt blanket, leaving the charcoal ink only in the concavas of the matted protruding parts which correspond to tracheal parts of the pattern. The charcoal ink was identical with the ink used in Example 13.

A melamine decorative laminate was formed, using the press plate and a titan paper printed with an oak tracheal pattern and impregnated with a melamine formaldehyde resin. The laminate thus obtained had large recessed tracheal parts which were colored charcoal and a very stereographic appearance. Its surface strikingly resembled that of a real oak veneer with the so-called "antique finish".

The effects of the present invention will now be summerized. The decorative laminate of the present invention has the following effects and advantages:

(a) The surface of the decorative laminate obtained has a soft gloss (luster) which extremely resembles the surface of pottery and has a three-dimensional pattern on the surface which corresponds to the smooth surface of the enamel layer formed by firing the enamel layer of the press plate. The decorative laminate thus obtained has an outer appearance which extremely resembles that of natural stone or pottery. A decorative laminate which resembles an enamel layer and which has a lustar and a three-dimensional pattern similar to those of the enamel layer is obtained even when a colorant of single color is used.

(b) A decorative laminate with protruding parts and recessed parts forming a continuous sinusoidally curved surface can be obtained. Since this decorative laminate does not have sharp edges in the pattern, it is suitable as a decorative laminate resembling enamel or pottery. Further, dust tends not to collect on the surface of the laminate and is easy to remove even when it has collected on the surface.

(c) A decorative laminate having shiny protruding parts and matted recessed parts can be obtained. This type of decorative laminated sheet could not be obtained with a metal press plate manufactured by a conventional etching method or the like. This decorative laminate is suitable for patterns of tile or enamel design.

(d) A decorative laminate having matted and colored recessed parts can be obtained. This decorative laminate is suitable for patterns of wood grain having tracheal parts or for tile patterns.

The manufacturing method of the decorative laminate of the present invention has the following effects or advantages:

(a) A release sheet need not be used in manufacturing a decorative laminate since the mold releasing properties of the enamel layer on the surface of the molding pate from the resin are greatly superior.

(b) The press plate having an enamal layer can be prepared with ease without requiring complicated processes such as etching and abrasion, resulting in economical manufacture.

(c) In manufacturing a melamine decorative laminate in general, pressures of 50 - 120 kg/cm^2 and temperature up to 140 - 160°C are required. Since the embossing plate used in the present invention is fired at a temperature of 500 - 1,000°C, it can easily withstand the above-mentioned pressure and heat. The service life of this embossing plate is therefore indefinitely long.

(d) When an enamal layer is formed on both surfaces of the press plate, warping of the enamel layer may be prevented in the firing process of the enamel layer and the pressing process of the decorative laminate. Further, if a three-dimensional pattern is formed on the enamel layers on both surfaces of the press plate, molding of a decorative laminate may be performed on both surfaces so that the manufacturing efficiency is improved.

(e) Since the enamel layer has better thermal conductivity than a conventional resin press plate, the manufacturing efficiency is improved.

(f) Since the three-dimensional pattern of the enamel layer consists of smooth curves, dust tends not to collect thereon, and is easy to wipe off when it has collected.

CLAIMS

1. A decorative laminate of thermosetting resin wherein a three-dimensional pattern on its surface consists of protruding parts and recessed parts forming smooth curves.

2. A decorative laminate as claimed in claim 1, wherein the protruding parts and the recessed parts of the surface consist of continuous curves.

3. A decorative laminate as claimed in claim 1, which is manufactured by a press plate having an enamel layer on its surface.

4. A decorative laminate as claimed in claim 2, wherein the recessed parts and the protruding parts from horizontally symmetrical curves.

5. A decorative laminate as claimed in claim 1, wherein more than one recessed parts having different depths are formed on the surface.

6. A decorative laminate as claimed in claim 1, which has a three-dimensional pattern on the surface, protruding parts of which are smooth and the bottoms of the recessed parts of which are matted.

7. A decorative laminate as claimed in claim 6, wherein the shoulder parts of said protruding parts form smooth curves.

8. A decorative laminate as claimed in claim 7, wherein the pattern is of a tile or enamel design.

9. A decorative laminate as claimed in claim 6, wherein a colorant is attached to the bottoms of said recessed parts.

10. A decorative laminate as claimed in claim 9, wherein the pattern is wood grain.

11. A decorative laminate as claimed in claim 9, wherein said recessed parts are all colored a single color.

12. A decorative laminate as claimed in claim 9, wherein said recessed parts are colored at least two colors.

13. A method for manufacturing a decorative laminate including a step of hot pressing a decorative laminate elements using a press plate, characterized in that the press plate having an enamel layer joined to the surface of a metal substrate is used.

14. A method as claimed in claim 13, wherein a smooth three-dimensional pattern is formed on the surface of said enamel layer.

15. A method as claimed in claim 13, wherein said enamel layer is formed by adding water and a mill addition agent to glass frit, kneading the mixture, coating it on a metal substrate and firing the coated layer.

16. A method as claimed in claim 13, wherein a press plate is used which is prepared by forming a protruding parts after printing a pattern by frit ink containing glass on the enamel layer and firing it.

17. A method as claimed in claim 16, wherein protruding parts of at least two different heights are formed.

18. A method as claimed in claim 16, wherein a ground coat layer and a cover coat enamel layer are formed on a metal substrate and said protruding parts are formed on the cover coat enamel layer.

19. A method as claimed in claim 16 or 17, wherein said protruding parts are matted by mixing a matting agent in said frit ink for forming said protruding parts.

20. A method as claimed in claim 19, wherein a colorant is held only at the matted parts of said

protruding parts of the press plate during hot pressing a decorative laminate element so that the recessed parts of the decorative laminate are melted and colored.

21. A method as claimed in claim 20, wherein said colorant includes a coloring component and, as a binder, a resin which is the same as a resin used in the decorative laminate or a resin which is compatible with said resin and cures at a temperature lower than said resin.

22. A decorative laminate, substantially as hereinbefore described with reference to the accompanying drawings and Examples.

23. A method for manufacturing a decorative laminate, substantially as hereinbefore described with reference to the accompanying drawings and Examples.

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